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Electrical Property and Antibacterial Effect of Fly Ash on the Viability of Cariogenic Oral Microorganisms

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From viewpoint of recycle of industry waste, the electrical and electrochemical characteristics of pyrolyzed fly ash and their applications have been investigated. Pristine fly ash inherently has a porous structure of carbon and even after high heat treatment, the porosity is maintained. Pyrolyzed fly ash used as the negative electrodes in rechargeable batteries shows good stability and high Coulombic efficiency in charge-discharge cycles in LiClO4/PC. We demonstrate the possibility to identify the species of oral microorganisms and reduce their activity and colony number by fly ashes.

KEYWORDS：fly ash, battery, Li ion, oral microorganism, antibacterial effect

フライアッシュの電気特性と口腔内細菌への抗菌効果

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火力発電所燃焼灰フライアッシュの電子物性及び電気化学的特性とその応用に関して検討を行った。フライアッシュは元々多孔性の構造を有しており、高温焼成後も多孔性を保持している。充放電試験において負極試料として用いられたフライアッシュは安定な充放電電位、極めて高いクーロン率など、優れた二次電池特性を示した。フライアッシュを用いた口腔内細菌の菌種の同定及び抗菌効果の可能性を提案する。

1.Introduction

Carbon materials have been widely used so far for personal and industrial applications such as electrode material for batteries, electrodes for motors, resistors, adsorbent, fibers, fuels, charcoal, painting material, etc. Recently new types of carbon materials such as fullerene C_{60} and carbon nano-tube have been discovered and attracted much attention from both the fundamental and practical viewpoints. We have also proposed new type of periodic porous carbon materials with pores of nano-scale size.

On the other hand, as the waste of power plants utilizing petroleum or coal as fuels, a lot of carbon materials have been formed and considered to be troublesome materials for our environment. Recently we have noticed that such carbons wastes named as fly ash have porous nature of structure and started to study from the fundamental viewpoint. On the other hands, we have explored the effective use of the fly ash for the practical applications[1)].

We have also studied electrochemical characteristics of oral cariogenic streptococci and the effect of metals and metal oxides on the streptococci to explore the possibility to identify the species of streptococcus and reduce the number of streptococci [2~6)].

In this paper, we discuss on the electrical property of fly ash, characteristics of fly ash as electrode material for the secondary battery and the antibacterial effect of the fly ash on the viability of the several oral microorganisms.

2.Experiment

In this study, the carbon content in pristine fly ash at the thermal power station is about 95%. Pristine fly ash inherently contains some amount of metals such as Ni and Fe that are used as catalysts to accelerate the growth of graphite layers. This fly ash was pyrolyzed at various temperatures for 1 h in a high-purity Ar atmosphere. The samples for electronic measurement were pressed into a sheet at 400kgf・cm^{-2}. The electrical conductivity and its temperature dependence were measured by a conventional four-probe technique using a Quantum Design PPMS. Electron microscope images of the morphology of pristine and pyrolyzed fly ashes were obtained by a scanning electron microscope (SEM) (S-2100A, Hitachi).

For preparation of a pellet - type electrode, fly ashes were mixed with 10wt% Teflon powder and pressed on a Ni mesh at 100kgf・cm^{-2}. A Lithium metal plate served as the counter and reference electrodes. The electrolytes used in this study were a 1M or 2M solution of $LiClO_4$ in a propylene carbonate (PC) in the case of pyrolyzed fly ashes with the HTTs of below 1400°C and a 1M solution of $LiPF_6$ in a 7 : 3 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) by volume in the case of pyrolyzed fly ashes with an HTT of 2800°C. Electrochemical measurements, including charge-discharge test were carried out using a beaker-type cell at room temperature in an argon-filled glove box (Miwa, MDB-1-B+MS80).

In this study, microorganisms such as Actinomyces viscosus (*A.v*), Streptococcus faceium (*S.f*), Streptococcus mitis (*S.m*), Streptococcus sanguis (*S.s*), Lactobacillus acidophilus (*L.a*) and Lactobacillus casei (*L.c*) were used. For the pre-cultivation of these resident floras, Ttypticase soy broth (TSB; Becton Disckinson and Co., Cockeysville, MD, U.S.A.) was used. After 48 hr, the cultured medium which was in the logarithmic phase was diluted and centrifuged. The precipitated microorganisms were washed with a small amount of phosphorus buffer and recentrifuged. These obtained microorganisms were dispersed in a neutral phosphorus buffer solution (pH7). Concentration of each microorganism in the above solution containing fly ash (concentration ratio: 0.1%) was 1 x 10^5 CFU (colony forming unit)/ml. Cultivation of the suspensions in an aerobic growth chamber, at 37°C, 55% relative humidity. Samples of the treated suspensions were incubated on TS agar plates. After 48 hr of cultivation at 37°C, the number of viability cells was counted.

3. Results and discussion

3-1 Electrical property of fly ash

Figure 1 indicates the scanning electron microscope images of the pristine and pyrolyzed fly ashes. As evident in this figure, fly ash contains many small pores of micro- and nano- scales in diameters. Even after a heat treatment at 2600°C, pyrolyzed fly ash maintains porosity and the surface of the pyrolyzed fly ash is more smooth than that of pristine fly ash.

The normalized temperature dependence of resistivity $\rho_r(T) = \rho(T)/\rho(200K)$ in pristine and pyrolyzed fly ashes is presented in Fig.2. The resistivity of the fly ash does not exponentially decrease with temperature. In the critical region of metal-insulator transition, the temperature dependence of resistivity obeys the power low dependence as given by

$$\rho(T) \propto T^{-\beta} \qquad (1)$$

, where β lies within the range $1/3 < \beta < 1$ [7]. These β values of the pristine fly ash and pyrolyzed fly ashes with the heat treatment temperatures (HTTs) of 1400 and 2600°C were evaluated from the slope of the straight lines in the Fig.2 to be 0.32, 0.17 and 0.17, respectively. In general, the conduction process is metallic if $\beta < 1/3$. The conduction process between particles of the fly ash becomes more metallic with increasing the HTT.

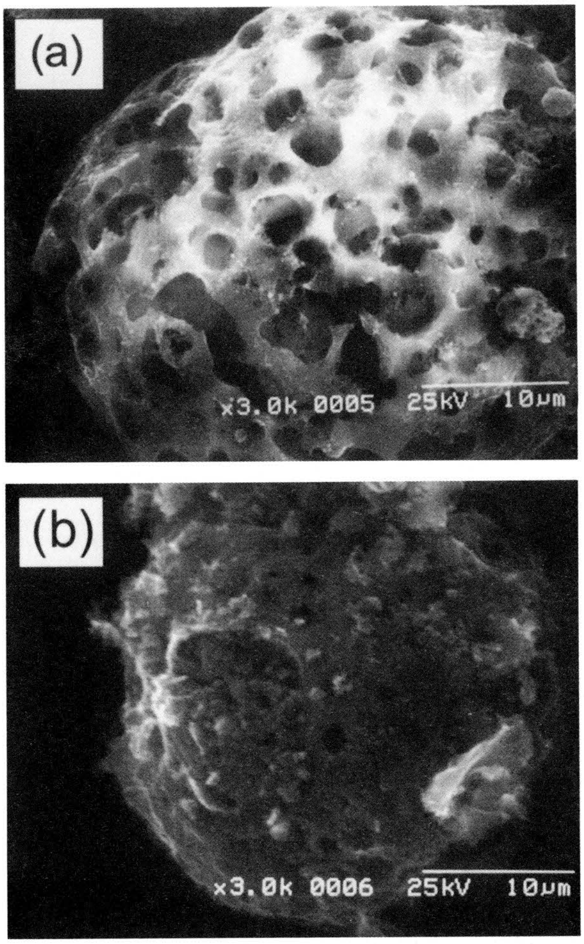

Fig.1: Scanning electron microscope images of (a) a pristine fry ash and (b) a pyrolized fly ash with a heat treatment temperature (HTT) of 2600oC.

3-2 Characteristics of fly ash as electrode material of secondary battery

From the viewpoint of the recycle of industry waste, we have also investigated the electrochemical properties of a pristine fly ash and pyrolyzed fly ashes with various HTTs as negative electrode materials of a lithium ion secondary battery. Figure 3 shows the third

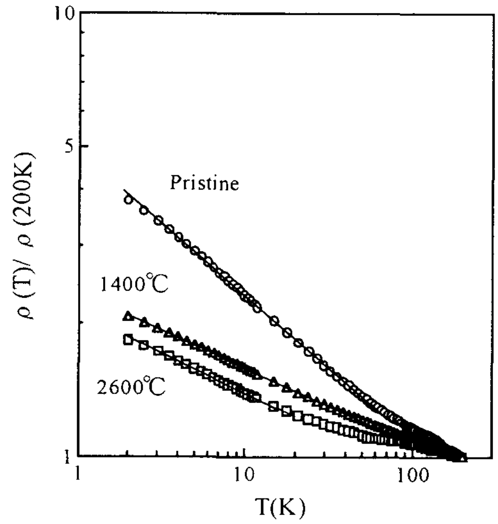

Fig.2: Normalized temperature dependence of resistivity rr (T) =r(T) /r(200 K) in a pristine fly ash and pyrolized fly ashes with the HTTs of 1400 and 2600°C.

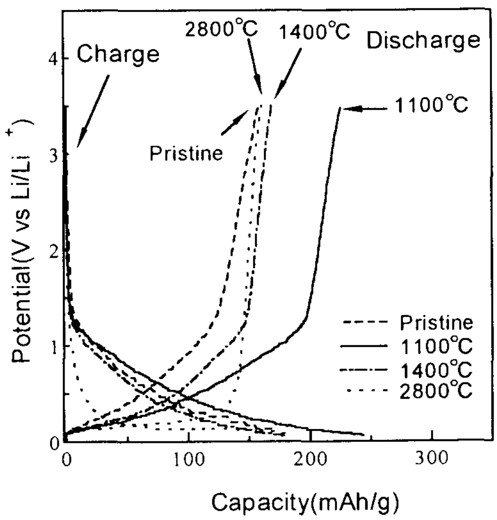

Fig.3: Charge-discharge profiles at the third cycle for pristine and pyrolized fly ashes with the HTTs of 1100, 1400 and 2800°C. The charge-discharge test was employed under the constant current corresponding to 20mA/g.

charge-discharge profiles of the pristine fly ash and the pyrolyzed fly ashes with HTTs of 1100, 1400 and 2800°C. The charge-discharge test was employed under the constant current corresponding to 20mA/g. The discharge capacity of pyrolyzed fly ash with an HTT of 1100°C is the highest. That is, the charge-discharge characteristic of fly ash can be improved by pyrolysis. The discharge capacities of the pristine fly ash and the pyrolyzed fly ashes with the HTT of 1100, 1400 and 2800°C were about 156, 223, 168 and 161 mAh/g, respectively. In all cases, the Coulombic efficiency is more than 90 %. As graphitization progresses, the curve of the pyrolyzed fly ash with the HTT of 2800°C is flattest in the region of about 0V vs the Li electrode, as is generally known for well-ordered graphite.

3-3 Antibacterial effect of fly ash on the viability of the various oral microorganisms

Figures 4, 5 and 6 show the change in the viability of the oral microorganisms such as *A.v*, *S.f*, *S.m*, *S.s*, *L.a* and *L.c* with the fly ashes. As evident in Fig.4, the number of viability cells of *A.v* decreases with increasing time. In the case of the oral microorganisms such as *S.m* and *S.s* as shown in Fig. 5, the number of viability cells markedly decreases with increasing time. While, the number of viability cell of *S.f* does not drastically decrease. Especially, in the case of *L.a*, the number of viability cells is maintained after 3 hours. It should be noted that except for *L.a*, the livability of all other oral microorganisms such as *A.v*, *S.f*, *S.m*, *S.s* and *L.c* decreases with increasing time.

These results clearly indicate that the fly ash is effective for reducing the density and activity of oral microorganisms. It should also be mentioned that the selectivity of the species of oral microorganisms exists in the effect of fly ash.

The activity of oral microorganisms seems to be confined in micro pores of fly ash, resulting in the suppression of the growth of oral microorganisms. It is not clear whether the oral microorganism is completely killed or just the growth is hindered at this stage.

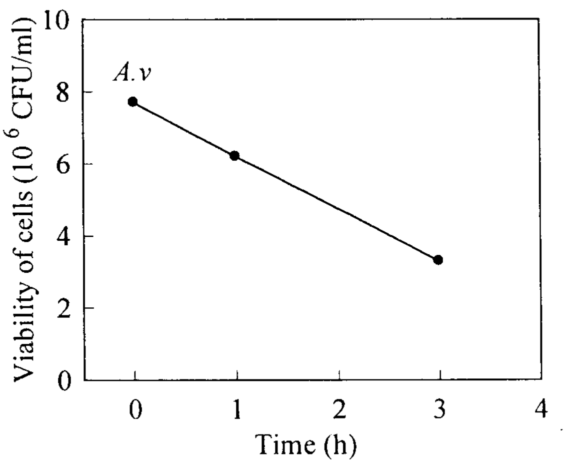

Fig.4: The change in the viability of Actinomyces viscosus (*A.v*) with the fly ash.

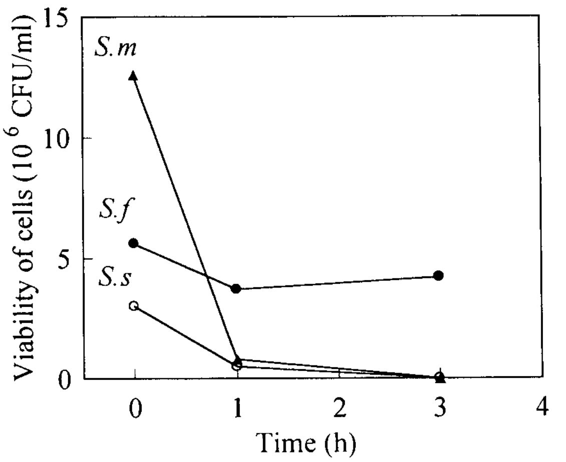

Fig.5: The change in the viability of oral microorganisms such as Streptococcus faceium (*S.f*), Streptococcus mitis (*S.m*) and Streptococcus sanguis (*S.s*) with the fly ash.

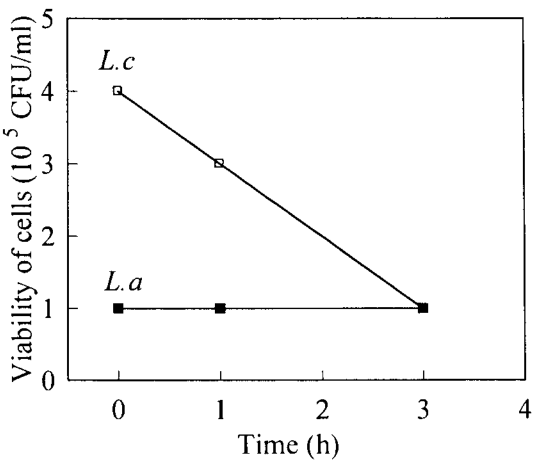

Fig.6: The change in the viability of oral microorganisms such as Lactobacillus acidophilus (*L.a*) and Lactobacillus casei (*L.c*) with the fly ash.

4. Conclusion

Pristine and pyrolyzed fly ashes contain many small pores of micro- and nano- scale sizes in diameters. The electrodes of pyrolized fly ash showed good stability and high Coulombic efficiencies in charge-discharge cycles in $LiClO_4$/PC. From the viewpoints of recycle of industry waste, we propose to apply the fly ash to a negative electrode of lithium ion secondary battery. We demonstrate the possibility to identify the species of oral microorganisms and reduce the number of those by using fly ashes.

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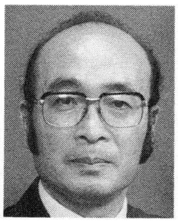

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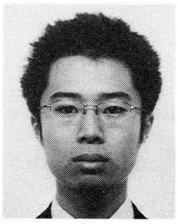

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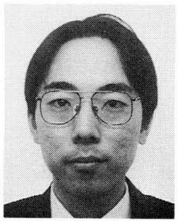

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